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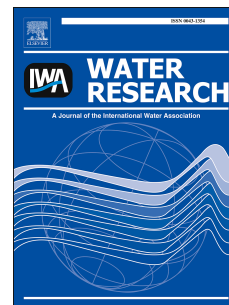
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Recovery of ammonia and sulfate from waste streams and bioenergy production via bipolar bioelectrodialysis

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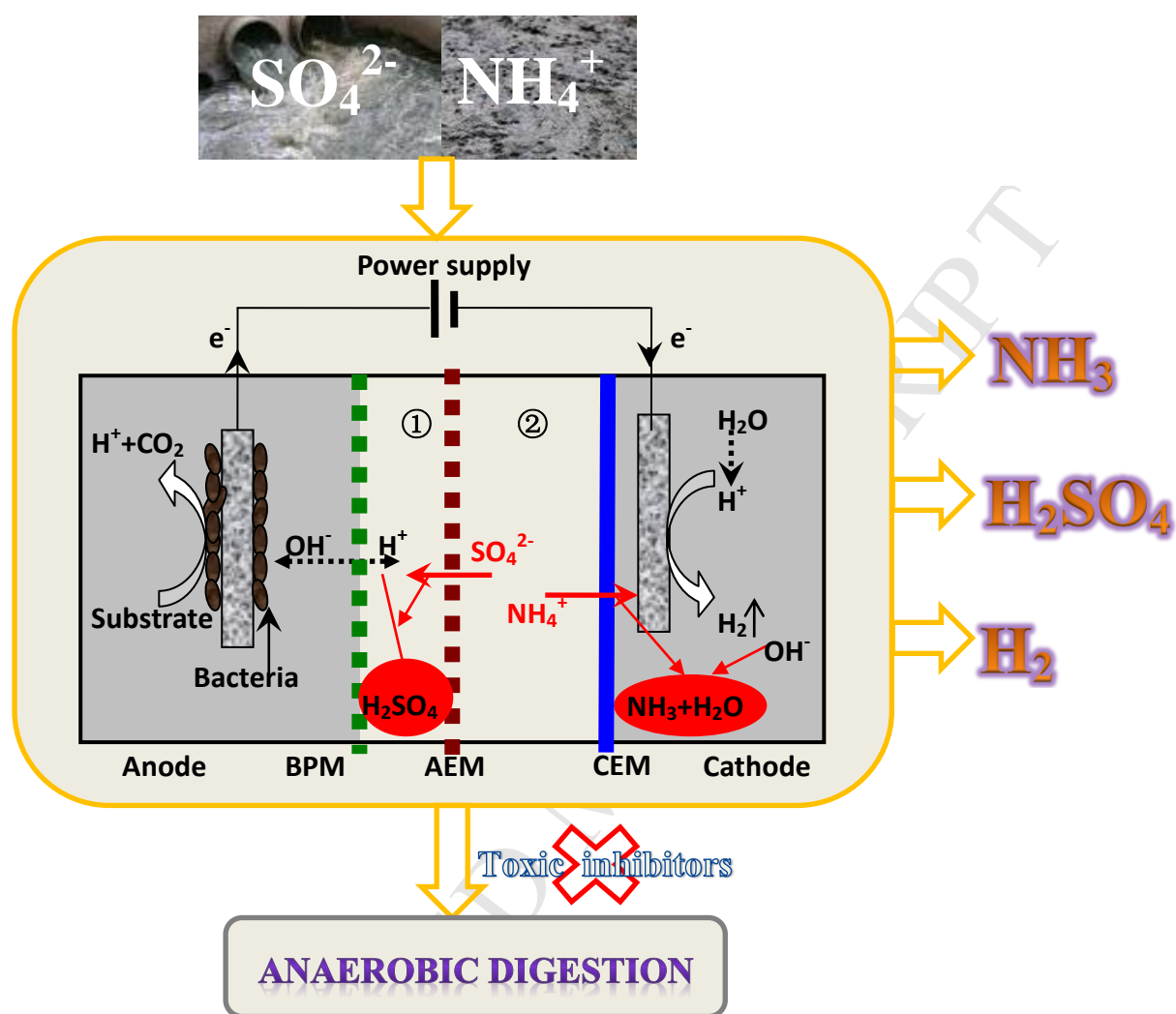
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3 Recovery of ammonia and sulfate from waste  
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5 bioelectrodialysis

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**Abstract**

Ammonia and sulfate, which are prevalent pollutants in agricultural and industrial wastewaters, can cause serious inhibition in several biological treatment processes, such as anaerobic digestion. In this study, a novel bioelectrochemical approach termed bipolar bioelectrodialysis was developed to recover ammonia and sulfate from waste streams and thereby counteracting their toxicity during anaerobic digestion. Furthermore, hydrogen production and wastewater treatment were also accomplished. At an applied voltage of 1.2 V, nitrogen and sulfate fluxes of 5.1 g  $\text{NH}_4^+\text{-N}/\text{m}^2/\text{d}$  and 18.9 g  $\text{SO}_4^{2-}/\text{m}^2/\text{d}$  were obtained, resulting in a Coulombic and current efficiencies of 23.6% and 77.4%, respectively. Meanwhile,  $\text{H}_2$  production of 0.29 L/L/d was achieved. Gas recirculation at the cathode increased the nitrogen and sulfate fluxes by 2.3 times. The applied voltage, initial  $(\text{NH}_4)_2\text{SO}_4$  concentrations and coexistence of other ions were affecting the system performance. The energy balance revealed that net energy ( $\geq 16.8$  kWh/kg-N recovered or  $\geq 4.8$  kWh/kg- $\text{H}_2\text{SO}_4$  recovered) was produced at all the applied voltages (0.8-1.4 V). Furthermore, the applicability of bipolar bioelectrodialysis was successfully demonstrated with cattle manure. The results provide new possibilities for development of cost-effective technologies, capable of waste resources recovery and renewable energy production.

**Keywords:** Bipolar bioelectrodialysis; Bioelectrochemical system; Ammonia; Sulfate; Resources recovery; Waste streams

## 1. Introduction

Anaerobic digestion is an attractive technology widely used for organic waste treatment and production of energy in the form of biogas (Weiland, 2010). However, the stability of the processes is hard to maintain due to a wide variety of toxic substances, among which free ammonia ( $\text{NH}_3$ ) and hydrogen sulphide ( $\text{H}_2\text{S}$ ) produced from sulfate reduction are two most significant inhibitors (Angelidaki and Ahring, 1994; Siles et al., 2010). Ammonia ( $\text{NH}_3/\text{NH}_4^+$ ) and sulfate ( $\text{SO}_4^{2-}$ ) are often found at high levels ( $\geq 3\text{ g NH}_4^+\text{-N/L}$  and up to  $13\text{ g SO}_4^{2-}\text{-S/L}$ , respectively) in the livestock manures and industry residues (Siles et al., 2010). As notorious environmental pollutants, these substances are often found in concentrations much higher than the inhibition levels. Inhibition can start at  $1.5\text{ g-NH}_4^+\text{-N/L}$  and/or  $1.4\text{ g-SO}_4^{2-}\text{/L}$  while 100% inhibition can be found at  $6\text{-}13\text{ g-NH}_4^+\text{-N/L}$  and/or  $1.8\text{ g-SO}_4^{2-}\text{/L}$  (El Hadj et al., 2009; Siles et al., 2010). Beside causing inhibition,  $\text{H}_2\text{S}$  derived from sulfate reduction can cause serious corrosion in compressors, gas storage tanks and engines, which need to be removed from biogas through energy-extensive processes (Ryckebosch et al., 2011). Several biological, chemical and physical techniques such as bioaugmentation, air stripping and chemical precipitation have been developed to remove or recover excess ammonia and thereby preventing the inhibition (Angelidaki and Ahring, 1994; Angeles De la Rubia et al., 2010; Ippersiel et al., 2012; Westerholm et al., 2012). However, most of the methods are uneconomical, requiring high energy input, have low efficiency, or need of additional chemicals. Most importantly, none of these methods can recover both ammonia and sulfate.

Recently, microbial electrochemical systems (MES) such as Microbial fuel cell (MFC) and microbial electrolysis cell (MEC) have been demonstrated as promising alternatives to conventional air-stripping for ammonia recovery (Kelly and He, 2014; Kuntke et al., 2012; Wu

and Modin, 2013). Though promising, there are still several challenges need to be addressed before field application. For example, anodic bacteria might be inhibited at high ammonia levels ( $>4 \text{ g NH}_4^+\text{-N/L}$ ) (Kim et al., 2011; Nam et al., 2010). To meet this challenge, microbial desalination cell (MDC) has recently been proposed to recover ammonia from anaerobic reactors (Zhang and Angelidaki, 2014). The principle of MDC has also been successfully applied to upconcentrate nutrients from diluted urine (Tice and Kim, 2014). Nevertheless, the dramatic pH drop in the anode during recovery needs to be prevented before practical application (Qu et al. 2012). Sulfate is potential electron acceptor in MES (Sun et al., 2009; Zhao et al., 2008), but direct recovery of sulfate (e.g., as sulfuric acid) has never been reported. Therefore, it is of great importance to explore the feasibility of sulfate recovery using MES. Furthermore, an advanced system that can combine ammonia and sulphide recovery should be pursued. An MES namely microbial electrolysis desalination and chemical production cell (MEDCC) was recently developed for water desalination, acid and alkali production (Chen et al., 2012). With an applied voltage ( $\sim 1.2 \text{ V}$ ),  $\text{Cl}^-$  and  $\text{Na}^+$  in the desalination chamber are driven across an anion exchange membrane (AEM) and a cation exchange membrane (CEM) into acid-production and cathode chambers, where they are recovered as  $\text{HCl}$  and  $\text{NaOH}$  (Chen et al., 2012). It has been reported that  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  have higher ionic conductivity and diffusivity to transport through membranes than that of  $\text{Na}^+$  and  $\text{Cl}^-$  (Tice and Kim, 2014). Thus,  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  could be captured in the form of  $\text{NH}_3$  (from  $\text{NH}_4^+$  and  $\text{OH}^-$ ) and  $\text{H}_2\text{SO}_4$ . In light of the above, the MEDCC could fulfill the requirements for ammonia and sulfate recovery, which has never been reported. Nevertheless, the extensive aeration in the cathode of MEDCC might be one of the key challenges for such new application.

In this study, we developed a bioelectrochemical system, called in the later as “bipolar bioelectrodialysis”, on the basis of MEDCC, for a brand new application with respect to simultaneous ammonia and sulfate recovery from waste streams and hydrogen production. Beside different application scopes, the main advantage of the bipolar bioelectrodialysis over the previous MEDCC is that the energy-intensive aeration at the cathode was replaced with cost-effective hydrogen production, which could offset the energy costs during recovery or be stored for further use. The objective of this study was to investigate the feasibility of the bipolar bioelectrodialysis system by varying operational parameters such as applied voltage, initial ammonia and sulfate concentration, and ionic species. Whereas the synthetic wastewater containing varied ammonia and sulfate concentrations was used for the investigation, also cattle manure was used as a proof of concept to demonstrate its applicability. This work demonstrates a new avenue to recover valuable resources from waste streams, produce bioenergy, and potentially prevent inhibitions during anaerobic digestion.

## **2. Materials and methods**

### **2.1 Experimental setup**

The bipolar bioelectrodialysis system composed of four chambers (inside dimensions 5 cm×5 cm×2 cm for each, Figure 1) was made of nonconductive polycarbonate. A bipolar membrane (BMP, fumasep® FBM, FuMA-Tech GmbH, Germany), an AEM (AMI 7001, Membrane international, NJ) and a CEM (CMI 7000, Membrane international, NJ) were placed between the anode and cathode chambers. The acid-production chamber was close to the anode side for sulfate recovery. The working chamber was close to the cathode side for receiving waste streams. The liquid volume of each chamber except anode was 40 mL. There were several openings on each chamber connected with rubber tube for feeding and sampling. The anode electrode was



made of a carbon fiber brush (5.0 cm diameter, 5.0 cm length, Mill-Rose, USA), which was pretreated at 450 °C for 30 min prior to use (Al Atrakchi 2014). The pretreated anode was pre-acclimated with mature biofilm in a MFC operated with wastewater. The cathode was a stainless steel woven mesh (4.0 x 4.0 cm, 0.24 mm wire diameter, 1.57 mm aperture, The Mesh Company, United Kingdom) coated with 0.5 mg/cm<sup>2</sup> Pt. All the electrical connection and electrode pretreatment were performed according to previous study (Zhang and Angelidaki, 2012a).

**Figure 1 is here**

## **2.2 Domestic wastewater, synthetic ammonia and sulfate-rich wastewater and cattle manure**

Domestic wastewater was collected from primary clarifier (Lyngby Wastewater Treatment Plant, Copenhagen, Denmark). The characteristics of the wastewater were as following: chemical oxygen demand (COD) 296 mg/L, pH 7.8, conductivity 1.4 mS/cm, nitrogen 0.07 g NH<sub>4</sub><sup>+</sup>-N/L, phosphorus 0.01 g PO<sub>4</sub><sup>2-</sup>-P/L, Na<sup>+</sup> 0.20 g/L, K<sup>+</sup> 0.07 g/L, Cl<sup>-</sup> 0.19 g/L, and SO<sub>4</sub><sup>2-</sup> 0.04 g/L. The synthetic wastewater was prepared with deionized water containing (pH 6.5): glucose 10 g/L, NaCl 0.10 g/L, MgCl<sub>6</sub>•H<sub>2</sub>O 0.10 g/L, CaCl<sub>2</sub> 0.05 g/L, NaHCO<sub>3</sub> 0.50 g/L and trace mineral metals solution (≤0.01 g/L in total). NH<sub>4</sub><sup>+</sup> and SO<sub>4</sub><sup>2-</sup> were added at different concentrations according to the tests. The cattle manure was collected from Vegger biogas plant, Denmark. The manure was sieved to remove coarse materials and stored at 4 °C before use. The characteristics of the manure were: pH 8.1, total solids 79.23 g/L, volatile solids 60.55 g/L, total Kjeldahl nitrogen 3.27 g/L, NH<sub>4</sub><sup>+</sup>-N 2.15 g/L, SO<sub>4</sub><sup>2-</sup> 0.03 g/L, Cl<sup>-</sup> 8.23 g/L, Ca<sup>2+</sup> 0.82g/L, K<sup>+</sup> 3.5 g/L, Na<sup>+</sup>0.83 g/L. The manure was amended with Na<sub>2</sub>SO<sub>4</sub> to mimic a mixture of ammonia and sulfate-rich waste, obtaining a final SO<sub>4</sub><sup>2-</sup> concentration of 5 g/L.

## **2.3 Reactor operation**

The domestic wastewater amended with acetate (2 g-COD/L in total) was recirculated from a feed reservoir (liquid volume of 500 mL) through anode at a recirculation rate of 50 mL/min using a peristaltic pump (OLE DICH, Instrucmentmakers APS, Denmark). Acetate was used here to eliminate the impact of substrate availability on the system performance. Synthetic wastewater or manure was fed into the working chamber. NaCl solution (0.1 M, pH 6.9) was used as catholyte. Unless stated otherwise, the gas phase of the cathode was internally recirculated at a rate of 50 mL/min. The feed reservoirs and all the chambers of the system were refilled when the current was lower than 0.2 mA, resulting in a single batch cycle. The reactor and reservoir were purged with nitrogen before starting each batch cycle. External voltage (0.8-1.4 V) was supplied by a power supply (HQ PS3003, Helmholtz Elektronik A/S, Denmark). The gas stream from cathode passed through adsorption bottle filled with 20 g/L boric acid before being collected into foil gas sampling bag. The acid solutions were renewed periodically. Control reactors either operated in open circuit or without gas recirculation were also set up. The external resistance was fixed at 10  $\Omega$ . All experiments were carried out in duplicate at ambient temperature (22 $\pm$ 3  $^{\circ}$ C).

#### 2.4 Electrochemical analysis and calculations

Kjeldahl nitrogen (KN),  $\text{NH}_4^+$  and COD were measured according to Standard method (APHA, 1998).  $\text{H}_2$  was analyzed by a GC-TCD fitted with a 4.5 m  $\times$  3 mm s-m stainless column packed with Molsieve SA (10/80).  $\text{Na}^+$  and  $\text{K}^+$  were measured using Flame atomic absorptions spectrophotometer (FAAS, Shimadzu).  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  were quantified by ion chromatography equipped with AS-9-HC column and conductivity detector (Dionex DX-300, Dionex Co., Sunnyvale, CA). pH was measured with a PHM 210 pH meter (Radiometer). Conductivity was determined using a CDM 83 conductivity meter (Radiometer).

The voltage ( $V$ ) was monitored every 30 min using a digital multimeter (Model 2700, Keithley Instruments, Inc., Cleveland, OH, USA). Current ( $I$ ), power ( $P=IV$ ) and Coulombic efficiency (CE) were calculated as previously described (Zhang and Angelidaki, 2012b). Current density was calculated based on the projected surface area of cathode. The ammonia flux ( $R_N$ ), sulfate flux ( $R_S$ ), cathodic hydrogen recovery ( $R_{H_2}$ ), current efficiency (CTE) and hydrogen production rate ( $H_{2pr}$ ) were calculated as below:

$$R_N = \frac{\Delta(m_N)}{At} \quad (1)$$

$$R_S = \frac{\Delta(m_S)}{At} \quad (2)$$

$$R_{H_2} = \frac{2FV_{H_2}}{RT \int_0^t Idt} \quad (3)$$

$$CTE = \frac{bF\Delta(m_S)}{\int_0^t Idt} \times 100\% \quad (4)$$

$$H_{2pr} = \frac{V_{H_2}}{tV} \quad (5)$$

Where  $\Delta(m_N)$  and  $\Delta(m_S)$  are the transported moles of ammonia and sulfate through membrane;  $t$  is operation time;  $A$  is the projected surface area of AEM or CEM.  $V$  is total liquid volume of cathode chamber;  $I$  is current;  $V_{H_2}$  is the measured hydrogen volume;  $T$  is the absolute temperature;  $R$  is the gas constant;  $F$  is Faraday's constant;  $b$  is the mole number of electrons transferred per mole of  $SO_4^{2-}$ .

### 3. Results and discussion

#### 3.1 The performance of bipolar bioelectrodialysis

The system performance was studied at batch mode at a voltage of 1.2 V. In the reactor without cathode gas recirculation, the concentration of ammonia in the working chamber decreased from 6 to 0.8 g-NH<sub>4</sub><sup>+</sup>-N/L, while the concentration of sulfate decreased from 20.6 to 2.5 g-SO<sub>4</sub><sup>2-</sup>/L after one batch cycle (266 h), resulting in a nitrogen and sulfate flux of 5.1 g-NH<sub>4</sub><sup>+</sup>-N/m<sup>2</sup>/d and 18.9 g-SO<sub>4</sub><sup>2-</sup>/m<sup>2</sup>/d (Figure 2A). When gas recirculation was employed at the cathode, the ammonia and sulfate fluxes increased to 11.7 g-NH<sub>4</sub><sup>+</sup>-N/m<sup>2</sup>/d and 40.7 g-SO<sub>4</sub><sup>2-</sup>/m<sup>2</sup>/d (Figure 2). In addition, gas circulation increased the final sulfate concentration in the recovery chamber, while it lowered the final ammonia concentration in the cathode. The enhanced ammonia and sulfate recovery when gas recirculation was applied at the cathode could be due to accelerated mass transfer and improved circuit current (Hou et al., 2014). The gas recirculation at cathode might also have resulted in NH<sub>3</sub> stripping from catholyte (discussed later), which could explain the reduced final ammonia concentration in the cathode. In the control reactor under open circuit, ammonia and sulfate concentrations in the working chamber decreased only slightly ( $\leq 19\%$ ), indicating the importance of current for driving the transportation of the ions. There were no significant changes in glucose concentration in either condition (data not shown), excluding the diffusion of glucose through membranes. Mass balance for the main ions was established to further elucidate the working mechanism of the bipolar bioelectrodialysis. As shown in Table 1, 85% of ammonia and 81% of sulfate were recovered without gas recirculation, while 90% and 93% were achieved with gas recirculation. In the reactor without gas recirculation, about 48% of the recovered ammonia remained at the cathode and another 52% was finally captured in the acid absorption bottle. However, only 20% of the recovered ammonia remained at the cathode with gas recirculation and another 80% was captured in the acid bottle, which supported our earlier assumption that NH<sub>3</sub> stripping from the cathode was enhanced with gas recirculation. The

concentrations of  $\text{Na}^+$  and  $\text{Cl}^-$  in the working chamber increased slightly after one batch cycle (Table 1). It was consistent with control experiment (open circuit), in which slight transportation of  $\text{Na}^+$  and  $\text{Cl}^-$  (1.9 and 2.5 g/L, data not shown) toward working chamber were detected along with slightly decrease of  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$ , respectively. The results imply that ion exchange might also contribute to the transportation of ammonia and sulfate (Jacobson et al., 2011).

**Figure 2 and Table 1 are here**

The pH in the different chambers is shown in Figure 2B. No significant changes in the anolyte pH were observed throughout the batch cycle, while the cathode pH increased from 6.9 to above 9.6 within 24 h and kept that level until end of operation in both reactors. The pH in the cathode with gas recirculation (9.99) was slightly higher than that without gas recirculation (9.80). The cathodic pH is the combination effect of hydrogen evolution and ammonia stripping. The hydrogen evolution could lead to the increase of pH while ammonia stripping could consume  $\text{OH}^-$  and decrease pH. The gas recirculation could accelerate both processes. According to the result here, it can be deduced that the contribution of gas recirculation to the improvement of hydrogen evolution was more effective than that to the air stripping. Thus, the cathode with gas recirculation showed relatively higher pH. The gas recirculation at cathode also led to significantly lower pH in the recovery and working chambers (pH 0.9 and pH 1.7, respectively) compared to that without gas recirculation (1.1 and 3.82, respectively). The drop of pH in the working chamber was probably due to the diffusion/leakage of  $\text{H}^+$  through AEM (Chen et al., 2012). To avoid the influence of low pH on the following anaerobic digestion, the effluent from the working chamber could be mixed with some other alkaline substrate or with the effluent from the cathode to adjust the pH. As shown in Figure 2C, the maximum stable current density in the reactor with cathode gas recirculation was approx.  $2.7 \text{ A/m}^2$ , which was higher than that without

gas recirculation ( $2.4 \text{ A/m}^2$ ). In both reactors, current density reached its maximum level at the beginning, and then decreased continuously until the end of batch cycle. This phenomenon was probably attributed to the ions depletion in the working chamber which increased the internal resistance (Cao et al. 2009). The COD consumption (approx. 50%) in the anode could also partly contribute to the decrease of current density. As expected from the current density,  $\text{H}_2$  production was also improved with gas recirculation at cathode. 146 mL of  $\text{H}_2$  was produced with gas recirculation while only 128 mL was produced without gas recirculation after a batch cycle. The increase in hydrogen production with gas recirculation was consistent with the increase of pH at the cathode (Figure 2B). In general, the reactor with cathode gas recirculation showed higher  $\text{RH}_2$ , CE and CTE compared to that without gas recirculation (Figure 2D). These parameters reached their maximum level at the beginning and then decreased with time in both reactors. For example,  $\text{RH}_2$ , CE and CTE reached to 92.7%, 36.3%, and 88.7% in the first 24 h in the reactor with gas recirculation. Overall, the results in this section demonstrated the feasibility of the bipolar bioelectrodialysis for ammonia and sulfate recovery along with  $\text{H}_2$  production.

**Figure 3 and Table 2 are here**

### **3.2 The system performance at different applied voltages**

Circuit current was the main driving force of ions transportation, thus it is of great importance to elucidate the correlation between different current levels and recovery process by varying the applied voltage. The system performance at different applied voltages is shown in Figure 3. All the parameters including current density,  $R_N$ ,  $R_S$ ,  $\text{H}_{2\text{pr}}$ , CE, and  $\text{RH}_2$  increased with the increasing of applied voltage (0.8-1.4 V). For example, current density,  $R_N$ ,  $R_S$ ,  $\text{H}_{2\text{pr}}$ , CE, and  $\text{RH}_2$  increased respectively by 76.5%, 158%, 154%, 350%, 114% and 70% after increasing the voltage from 0.8 to 1.4 V. It is likely that the increasing of system performance might continue at even higher

voltage. However, the electric energy consumption would probably increase with voltage and thereby affecting net energy gain. Therefore, energy balance analysis was made (Table 2). The analysis revealed that net energy ( $\geq 16.8$  kWh/kg-N or  $\geq 4.8$  kWh/kg-H<sub>2</sub>SO<sub>4</sub>) was produced during ammonia and sulfate ions recovery at all the voltages (0.8-1.4 V). The energy gain increased with the voltage till 1.2 V. However, further increasing voltage to 1.4 V decreased energy production due to increased electric energy consumption in the system. Thus, the optimum voltage for energy recovery in the bipolar bioelectrodialysis system was 1.2 V. The energy produced at 1.2 V with initial ammonia and sulfate concentration of 6 g-N/L and 20.6 g-SO<sub>4</sub><sup>2-</sup>/L was higher than that obtained with 4 g-N/L and 13.7 g-SO<sub>4</sub><sup>2-</sup>/L. The increased conductivity at relatively higher ammonia and sulfate concentration could be a possible explanation. It was also noticed that the gas recirculation at the cathode didn't reduce the overall energy gain. Instead, more energy was gained due to high H<sub>2</sub> production at the cathode. The net energy gained here was higher than that reported in the previous studies concerning MES with ammonia recovery (Kuntke et al., 2012; Wu and Modin, 2013, Zhang and Angelidaki, 2014). Beside the different operation conditions, sulfate recovery could improve energy production. In the light of above, the applied voltage was an important factor affecting the system performance and the system could with advantage be operated at 1.2 V. It should be noted that this preliminary energy analysis didn't include the purification costs for the recovered sulfuric acid, since presence of other ions (i.e., NaCl in this study) in the recovery chamber could be avoided in continuous operation. In that case, deionized water or low concentration of H<sub>2</sub>SO<sub>4</sub> instead of NaCl could be just needed at the beginning to initiate the process, but its feasibility needs to be further studied.

### 3.3 The effect of initial NH<sub>4</sub><sup>+</sup> and SO<sub>4</sub><sup>2-</sup> concentrations on system performance

(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> was added into the synthetic wastewater at different concentrations to explore the influence of initial ammonia and sulfate concentration on the system performance (Figure 4). Current density increased from 1.7 to 2.7 A/m<sup>2</sup> with the increasing of initial (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> concentrations from 9.4 to 28.3 g/L (corresponding to 2~6 g NH<sub>4</sub><sup>+</sup>-N/L or 6.9~20.6 g-SO<sub>4</sub><sup>2-</sup>/L). The high conductivity contributed by the high (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> concentration might explain the high current density. Along with current density, R<sub>N</sub>, R<sub>S</sub>, H<sub>2pr</sub>, CE, and RH<sub>2</sub> also increased with initial (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> concentration. For example, R<sub>N</sub> of 7.6g-N/m<sup>2</sup>/d, R<sub>S</sub> of 24.5 g-SO<sub>4</sub><sup>2-</sup>/m<sup>2</sup>/d, H<sub>2pr</sub> of 0.27 L/L/d, CE 19.6%, and RH<sub>2</sub> of 56.4% were obtained at (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> concentration of 9.4 g/L, while much higher values of 11.7 g-N/m<sup>2</sup>/d, 40.5 g-SO<sub>4</sub><sup>2-</sup>/m<sup>2</sup>/d, 0.54 L/L/d, 28.9%, and 68.6% were achieved at (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> concentration of 28.3 g/L. The results indicate that the bipolar bioelectrodialysis could be applicable to waste streams with wide range of ammonia and sulfate concentrations. The bipolar bioelectrodialysis was targeting the waste streams with high concentration of ammonia and sulfate which can cause severe inhibition during anaerobic digestion, such as livestock manures and industrial wastewaters (or mixture of two by co-digestion). Thus, the synthetic wastewater was used to mimic those waste streams. The system could also be applied to the wastewater with low level of ammonia and sulfate (e.g., domestic wastewater), which could be a new application for future study.

**Figure 4 is here**

### **3.4 The effect of other ionic species on NH<sub>4</sub><sup>+</sup> and SO<sub>4</sub><sup>2-</sup> transportation**

Although SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup> are dominant ions in ammonia and sulfate-rich wastewaters, other ions such as Cl<sup>-</sup> and Na<sup>+</sup> might also move through membranes and thereby affecting the recovery processes. Thus, Cl<sup>-</sup> and Na<sup>+</sup> (150 mM each) were added into the synthetic wastewater containing 300 mM NH<sub>4</sub><sup>+</sup> and 150 mM SO<sub>4</sub><sup>2-</sup> to investigate their impact on the system



285 performance (Figure 5). In the working chamber,  $\text{NH}_4^+$  concentration decreased sharply from  
 286 300 to 19 mM within 120 h, while  $\text{Na}^+$  concentration decreased slightly from 150 to 124 mM  
 287 during the same period. Thereafter,  $\text{Na}^+$  concentration decreased dramatically and at the end of  
 288 batch cycle approached a level lower than 24 mM. Similarly,  $\text{SO}_4^{2-}$  concentration in the working  
 289 chamber decreased fast in the first 72 h (150 to 57 mM), while  $\text{Cl}^-$  concentration was around 125  
 290 mM during this period. Nevertheless,  $\text{Cl}^-$  concentration decreased continuously along with  $\text{SO}_4^{2-}$   
 291 from 72 h till the end of the batch cycle. Correspondingly,  $\text{NH}_4^+$  transportation to the cathode  
 292 was faster than that of  $\text{Na}^+$ , while  $\text{SO}_4^{2-}$  transportation to the recovery chamber was faster than  
 293 that of  $\text{Cl}^-$  (Figure 5B). The initial lag period of the  $\text{Na}^+$  and  $\text{Cl}^-$  transportation could be due to the  
 294 lack of concentration gradient between the membrane. It has been reported that same level of  
 295 ionic concentration between membranes can prevent ions diffusion (Desloover et al., 2012). The  
 296 higher equivalent ionic conductivity of  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  over other ions (e.g.,  $\text{Na}^+$  and  $\text{Cl}^-$ ) could  
 297 also be responsible for the selective  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  transportation (Tice and Kim, 2014). Unlike  
 298  $\text{Na}^+$ , ammonia was continuously leaving from the reactor (cathode) in terms of volatile  $\text{NH}_3$ ,  
 299 which might be favorable for selective  $\text{NH}_4^+$  transportation. This could also explain the relatively  
 300 longer lag phase of  $\text{Na}^+$  transportation. It should be noted that current density,  $\text{H}_2$ , CE and  $\text{R}_{\text{H}_2}$   
 301 observed here (Figure S1, Supplementary data) was much higher than that without NaCl addition  
 302 in the working chamber shown in Figure 3 (at 1.2 V). This was probably due to the increased  
 303 conductivity after adding NaCl. Thus, the coexistence of other ions didn't affect the ammonia  
 304 recovery, but it may influence the purity of  $\text{H}_2\text{SO}_4$  recovered at the recovery chamber (e.g., in  
 305 terms of HCl). The acids mixture could be used directly in industries or further purified. It could  
 306 be interesting to investigate the effect of other cations such as  $\text{Ca}^{2+}$  and  $\text{K}^+$  which could also be  
 307 found in most of waste streams. However,  $\text{Ca}^{2+}$  and  $\text{K}^+$  are quite similar to  $\text{Na}^+$  in terms of

transportation property through cation exchange membrane. It can be expected that  $\text{Ca}^{2+}$  and  $\text{K}^{+}$  have similar effect as  $\text{Na}^{+}$  on the system. Thus, the ammonia transportation would not be adversely affected no matter which cation ( $\text{Ca}^{2+}$ ,  $\text{K}^{+}$ , or  $\text{Na}^{+}$ ) presented. Specialized anion exchange membranes that are selective for  $\text{NH}_4^{+}$  and  $\text{SO}_4^{2-}$  ions could be developed in future to enhance selective recovery from complex waste streams.

**Figure 5 is here**

### **3.5 The system performance with cattle manure**

The applicability of the bipolar bioelectrodialysis was further verified with cattle manure. As shown in Figure 6, the concentration of  $\text{NH}_4^{+}$  and  $\text{SO}_4^{2-}$  in the working chamber decreased continuously until the end of batch cycle, while constant accumulation of  $\text{NH}_4^{+}$  and  $\text{SO}_4^{2-}$  was observed respectively in the cathode and recovery chamber. Consistent with previous observation,  $\text{NH}_4^{+}$  concentration in the cathode was much lower than the level removed from the working chamber due to free  $\text{NH}_3$  volatilization. More than 94% of  $\text{NH}_4^{+}$  and  $\text{SO}_4^{2-}$  in the cattle manure were finally recovered at the end of batch cycle. Current density reached maximum level (approx.  $2.3 \text{ A/m}^2$ ) at the beginning and thereafter decreased to  $0.8 \text{ A/m}^2$  after 182 h, resulting in an average CE of 27.7%. The remained current density at the end of recovery process could be due to the presence of other ions in the cattle manure which support the conductivity inside of the system. Along with ammonia and sulfate recovery,  $\text{H}_2$  production at the cathode increased gradually to 150 mL with an average  $R_{\text{H}_2}$  of 68.2%. The above results demonstrated the applicability of the bipolar bioelectrodialysis to the complex waste streams. The cattle manure amended with  $\text{SO}_4^{2-}$  was used in this test, further investigation with waste streams originally containing both ammonia and sulfate (e.g., urine) may promote the industrial application of the

technology. Co-digestion of two waste streams rich either in ammonia or sulfate may also fit well with the application.

Figure 6 is here

#### 4. Conclusion

Ammonia and sulfide derived from sulfate reduction are two notorious toxic compounds in anaerobic digestion processes. Removal or recovery of these inhibitors is always energy-intensive and inefficient, and a method that can achieve simultaneous ammonia and sulfate recovery has never been reported so far. It was shown in this study that bipolar bioelectrodilysis was an attractive alternative method to recover ammonia and sulfate and produce hydrogen, allowing the counteraction of their toxicity during anaerobic digestion. The bipolar bioelectrodilysis offers several advantages over conventional methods: (1) This is the first technology which can recover two inhibitors (or its precursor) simultaneously; (2) In-situ recovery without additional chemicals. Instead, hydrogen was produced to make the process self-sustainable; (3) The recovered sulphuric acid could be used to capture ammonia which make the technology even economic feasible; (4) No risk of inhibition on exoelectrogens, as the waste will not be fed into the anode; (5) No need of further  $H_2S$  removal from the biogas, since its precursor (i.e., sulfate) is recovered, and thereby reducing the biogas upgrading costs; (6) Wastewater treatment can be accomplished through the oxidation in the anode. The extent of recovery could be further optimized by addressing the challenges related to materials (e.g., selective membrane), operation (continuous mode), and microbiology. Especially, the quality of the effluent in each chamber should be considered and optimized. The COD removal in the anode could be further improved by regulating the hydraulic retention time and other operational parameters (e.g., type of wastewater). The catholyte could be reused for several times, which needs to be further

studied. Furthermore, the NaCl solution could be replaced by deionized water or H<sub>2</sub>SO<sub>4</sub> as electrolyte in the recovery chamber in continuous operation to initiate the recovery process and thereby improving the purity of the recovered H<sub>2</sub>SO<sub>4</sub>. Besides, while the ratio of N/S was fixed in this study to prove the concept, the influence of different N/S ratios along with individual substance concentrations should be investigated in future to better understand the system. According to the results regarding different initial ammonia and sulfate concentrations, it can be expected that the system could also work at varied ammonia and sulfate ratios. In addition, the bipolar bioelectrodialysis could be linked to anaerobic digestion process for further exploring its effectiveness on biogas enhancement. Considering that large amount of world's biogas plants are suffering economic and energy losses caused by ammonia and sulfide inhibition, there is significant potential for bipolar bioelectrodialysis.

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**Table 1** Mass balance on the main ions

Test		AC	RC	WC	CC	AB <sup>d</sup>	Total	Balance (100%)		
1 <sup>a</sup>	NH <sub>4</sub> <sup>+</sup> (mg)	In	- <sup>b</sup>	0	308.6±1.1	0	0	308.6±1.1	98.3±0.5	
		out	-	0	41.1±0.3	128.6±0.6	133.7±0.3	303.4±0.6		
	SO <sub>4</sub> <sup>2-</sup> (mg)	In	-	0	822.9±0.7	0	0	822.9±0.7	97.7±0.3	
		out	-	668.0±0.4	136±0.7	0	0	804.0±1.5		
	Na <sup>+</sup> (mg)	In	-	92.0±2.9	0.4±0.1	92.0±2.9	0	184.4±2.9	95.7±7.5	
		out	-	88.0±5.7	36.4±5.7	52.0±11.3	0	176.4±11.3		
	Cl <sup>-</sup> (mg)	In	-	140.0±8.5	0.2±0.1	140.0±8.5	0	280.2±8.5	97.8±4.3	
		out	-	116.0±5.7	20.1±4.5	138.0±2.8	0	274.1±3.9		
	2 <sup>c</sup>	NH <sub>4</sub> <sup>+</sup> (mg)	In	-	0	308.6±1.1	0	0	308.6±1.1	98.0±4.1
			out	-	0	25.7±7.3	57.1±13.8	219.6±9.1	302.4±15.6	
SO <sub>4</sub> <sup>2-</sup> (mg)		In	-	0	822.9±0.7	0	0	822.9±0.7	99.6±4.5	
		out	-	764.0±19.8	56±16.9	0	0	820.0±36.8		
Na <sup>+</sup> (mg)		In	-	92.0±2.5	0.4±0.1	92.0±2.5	0	184.4±2.9	102.2±3.1	
		out	-	96.0±11.3	28.3±11.3	64.0±5.7	0	188.3±5.7		
Cl <sup>-</sup> (mg)		In	-	140.0±8.5	0.2±0.1	140.0±8.5	0	280.2±8.5	98.0±3.4	
		out	-	120±9.6	16.2±3.4	138.4±3.4	0	274.6±9.6		

<sup>a</sup> Without recirculation in the cathode. The data was taken at the end of batch run (266 h)

<sup>b</sup> The ions in the anolyte was not considered, as some of ions might be consumed and their migration to/from the other chambers could be ignored due to BPM separation.

<sup>c</sup> With recirculation in the cathode. The data was taken at the end of batch run (181 h)

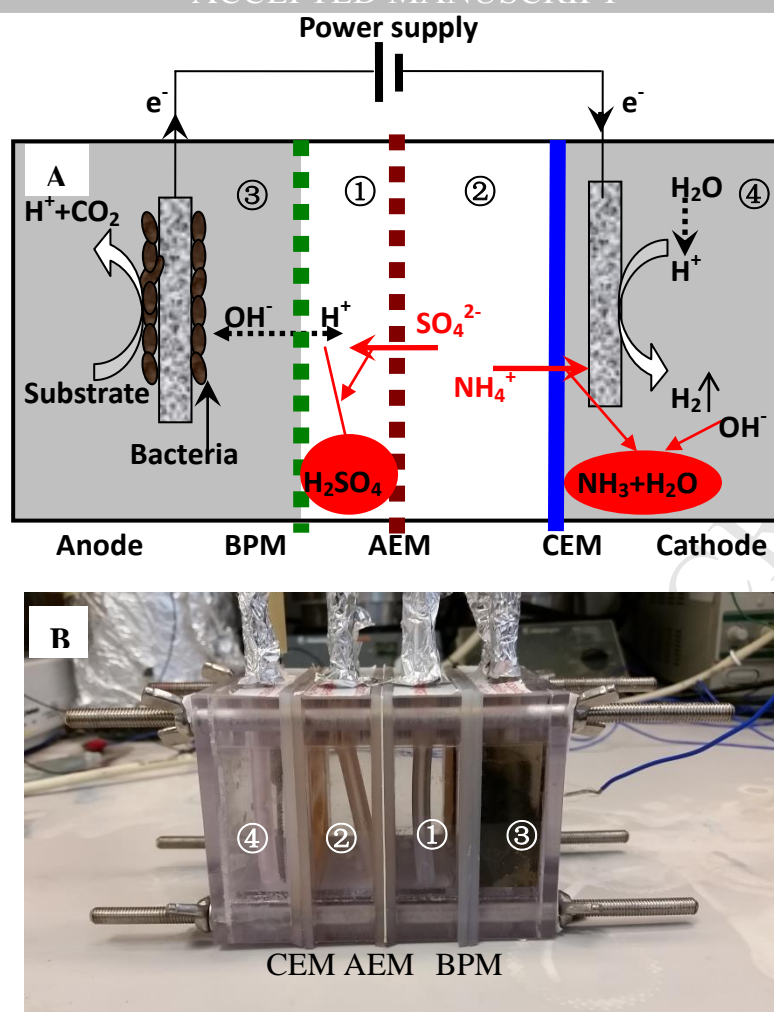
<sup>d</sup> Adsorption bottle filled with boric acid.



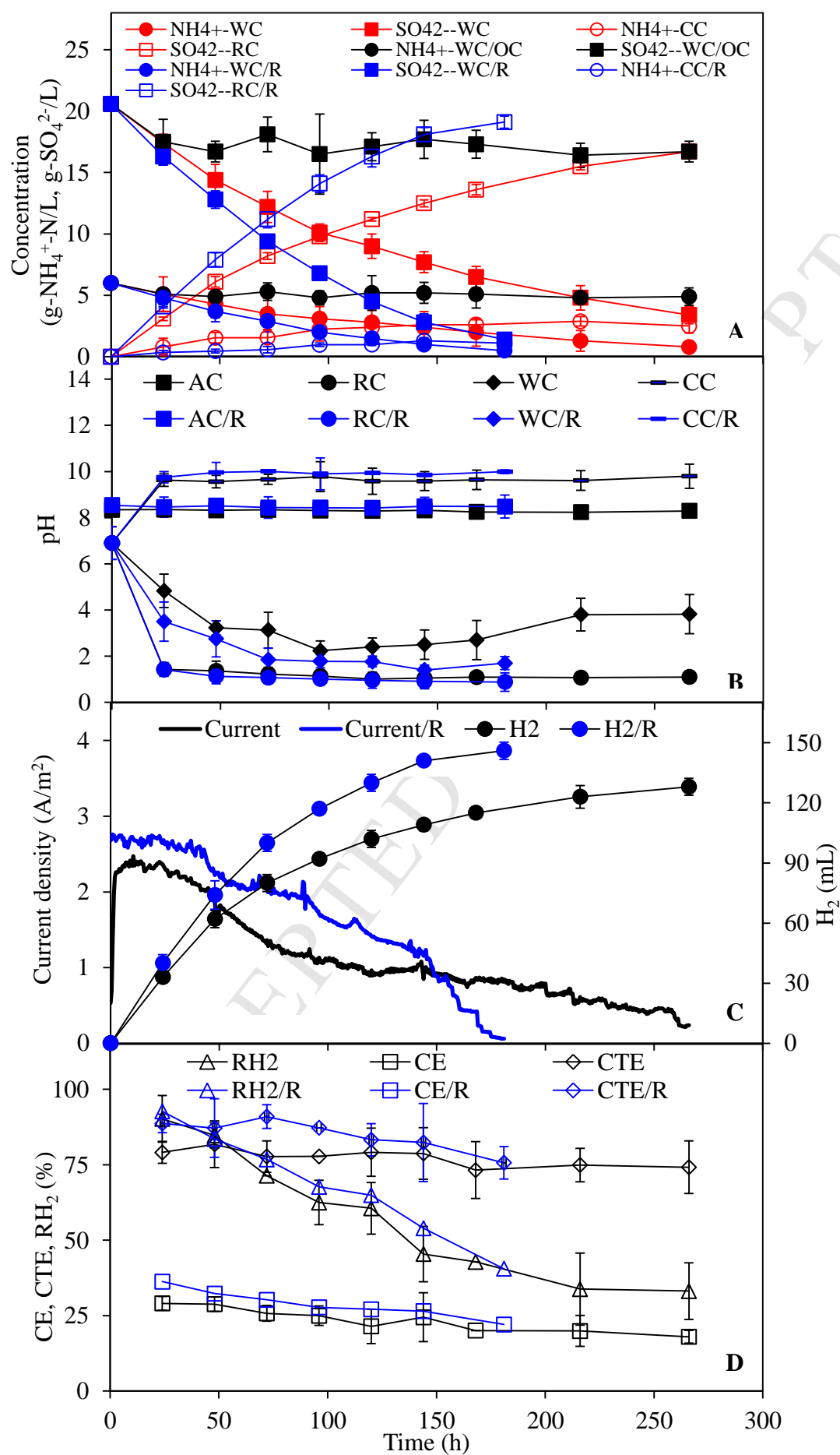
**Table 2** Energy balance analysis based on the batch test

Voltage (V)	Normalized Units	Input		Output			Net energy balance
		Electric energy <sup>a</sup>	Pumping <sup>b</sup>	NH <sub>3</sub> energy equiv <sup>c</sup>	H <sub>2</sub> SO <sub>4</sub> energy equiv <sup>d</sup>	H <sub>2</sub>	
0.8	kWh/kg-N	-2.04 <sup>i</sup>	-0.42	10.30	7.57 <sup>e</sup>	1.53	16.94
	kWh/kg-H <sub>2</sub> SO <sub>4</sub>	-0.59	-0.12	2.96 <sup>e</sup>	2.18	0.44	4.87
1.0	kWh/kg-N	-2.54	-0.27	10.30	7.58 <sup>e</sup>	1.92	16.99
	kWh/kg-H <sub>2</sub> SO <sub>4</sub>	-0.73	-0.08	2.96 <sup>e</sup>	2.18	0.55	4.88
1.2	kWh/kg-N	-2.95	-0.19	10.30	7.60 <sup>e</sup>	2.35	17.11
	kWh/kg-H <sub>2</sub> SO <sub>4</sub>	-0.85	-0.05	2.95 <sup>e</sup>	2.18	0.67	4.90
1.2 <sup>f</sup>	kWh/kg-N	-2.75	-0.16	10.30	7.69 <sup>e</sup>	2.40	17.48
	kWh/kg-H <sub>2</sub> SO <sub>4</sub>	-0.78	-0.04	2.92 <sup>e</sup>	2.18	0.68	4.96
1.2 <sup>g</sup>	kWh/kg-N	-2.67	- <sup>h</sup>	10.30	7.58 <sup>e</sup>	2.11	17.32
	kWh/kg-H <sub>2</sub> SO <sub>4</sub>	-0.77	-	2.96 <sup>e</sup>	2.18	0.61	4.98
1.4	kWh/kg-N	-3.56	-0.16	10.30	7.64 <sup>e</sup>	2.58	16.80
	kWh/kg-H <sub>2</sub> SO <sub>4</sub>	-1.02	-0.04	2.94 <sup>e</sup>	2.18	0.74	4.80

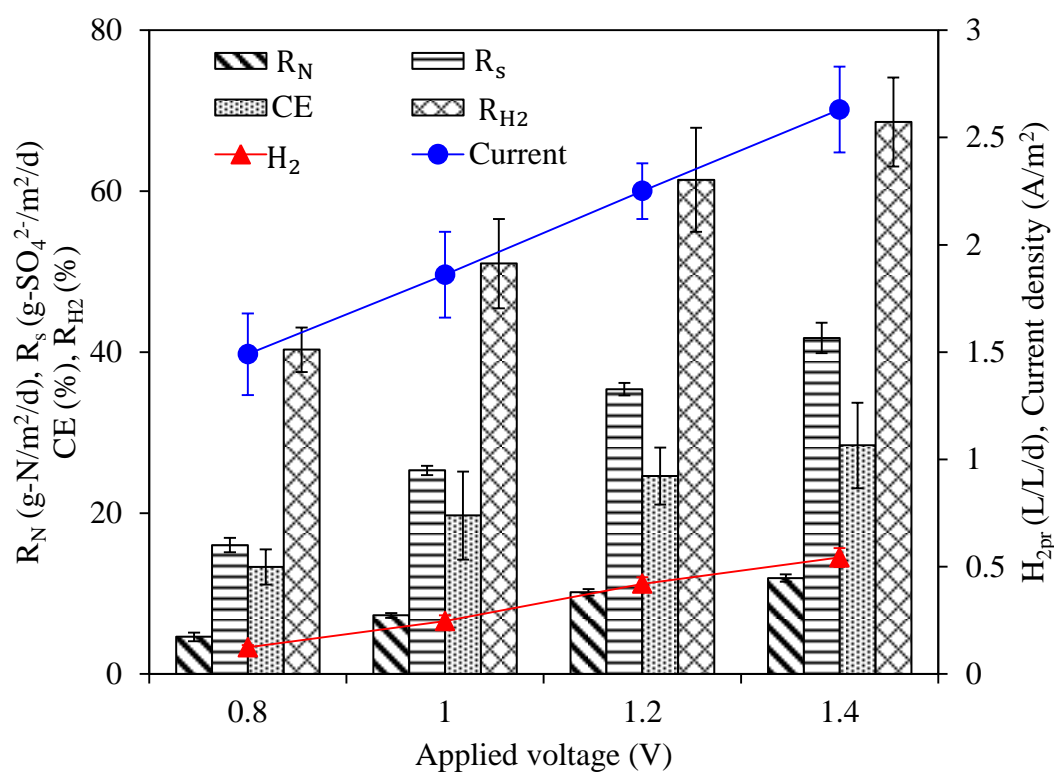
<sup>a</sup> Based on the current over the batch cycle<sup>b</sup> Estimated according to hydraulic head loss and theoretic equation (in Supplementary data).<sup>c</sup> Assumed energy consumption for Haber-Bosch process<sup>d</sup> Assumed energy consumption for wet sulfuric acid process<sup>e</sup> Calculated based on the mole ratio of recovered NH<sub>3</sub> and SO<sub>4</sub><sup>2-</sup> in each batch<sup>f</sup> The initial NH<sub>4</sub><sup>+</sup>-N and SO<sub>4</sub><sup>2-</sup> concentration in the WC was 6 and 20.6 g/L (mole ratio of 2:1).<sup>g</sup> The initial NH<sub>4</sub><sup>+</sup>-N and SO<sub>4</sub><sup>2-</sup> concentration in the WC was 6 and 20.6 g/L (mole ratio of 2:1), but without cathode recirculation.<sup>h</sup> not applicable<sup>i</sup> Minus means energy cost, while positive means energy gain



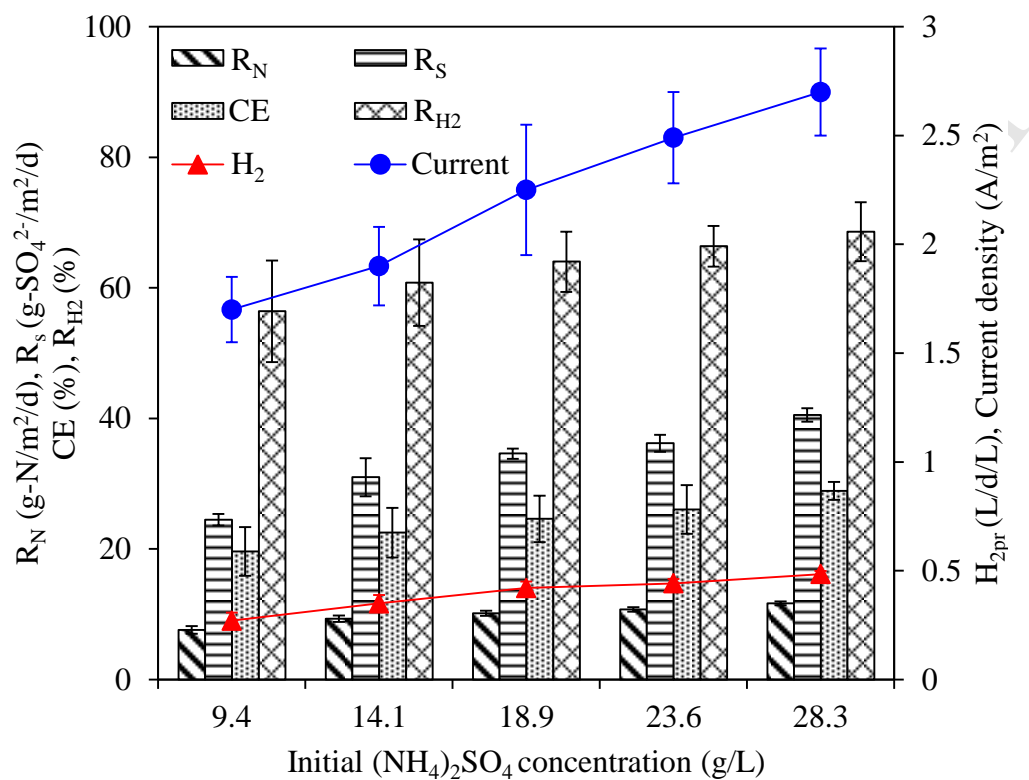
**Figure 1** Schematic illustration (A) and image (B) of the bipolar bioelectrodialysis from opposite view. ① Recovery chamber, ② Working chamber, ③ Anode, ④ Cathode.



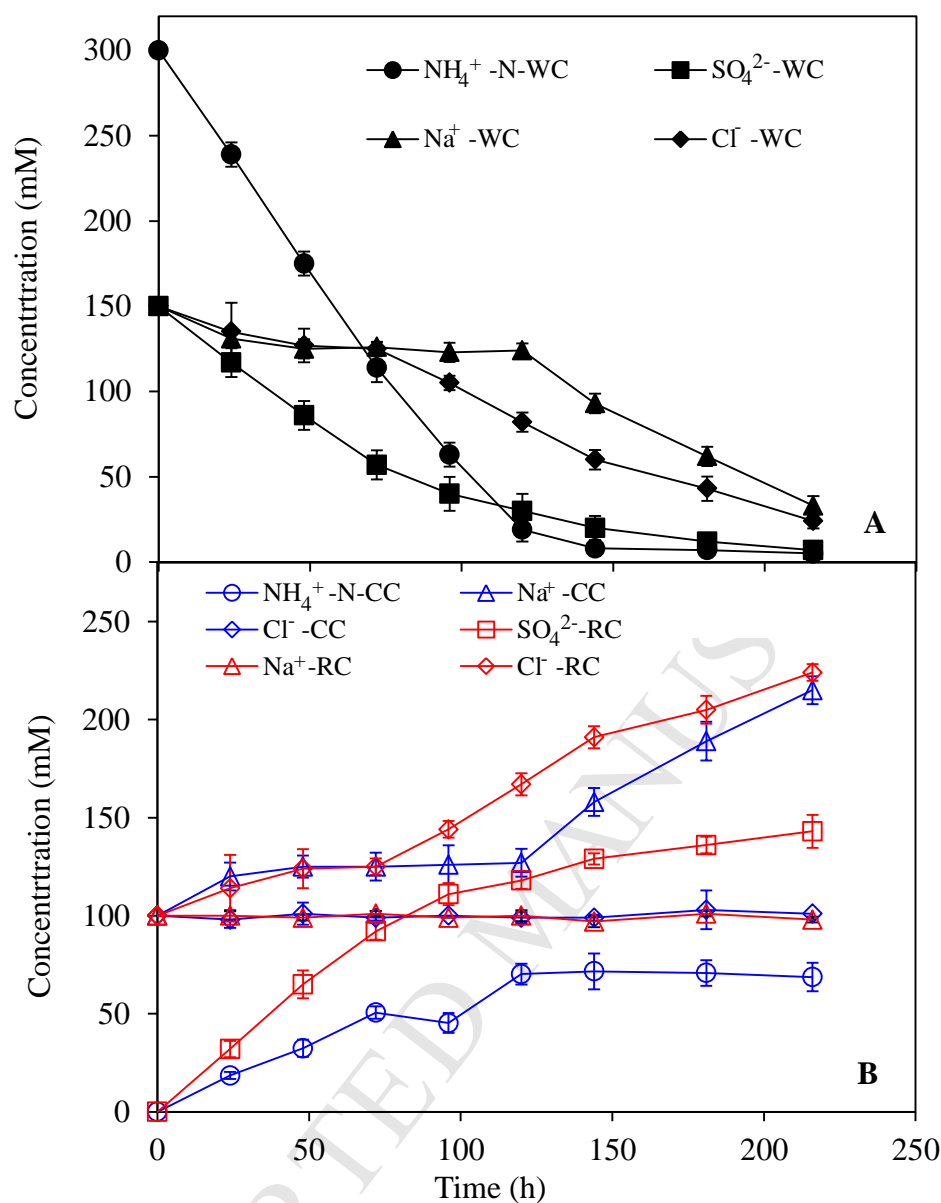
**Figure 2** Change of process performances with time. (A)  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  concentrations; (B) pH in different chambers; (C) Current and hydrogen production; (D) CE, CTE and RH2. AC, anode chamber; RC, recovery chamber; WC, working chamber; CC, cathode chamber; OC, open circuit; R, gas recirculation in the cathode.



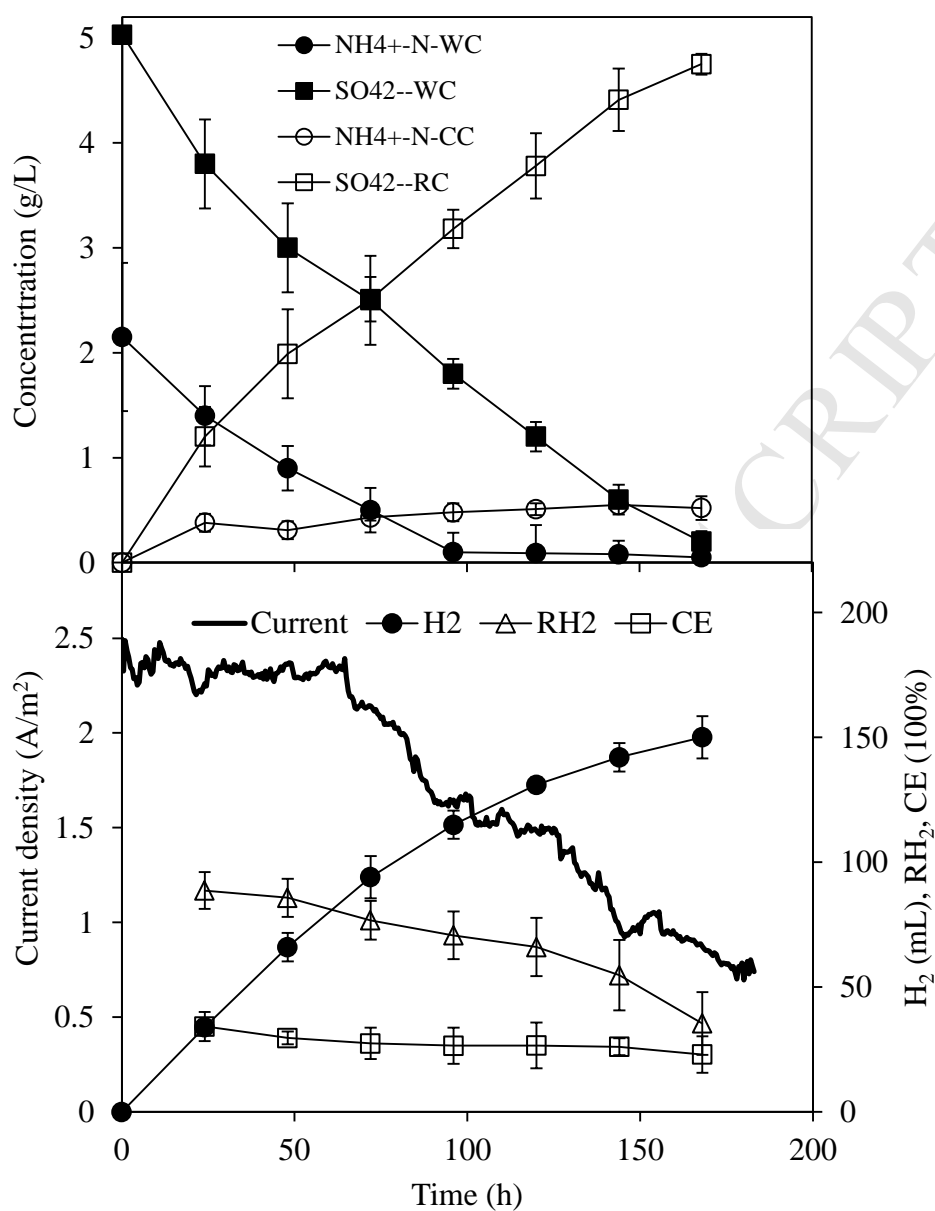
**Figure 3** Process performances at different applied voltages. The initial  $NH_4^+$ -N and  $SO_4^{2-}$  concentration in the WC was 4 and 13.7 g/L (mole ratio of 2:1).



**Figure 4** Process performances at different initial  $(\text{NH}_4)_2\text{SO}_4$  concentration. The applied voltage was 1.2 V.



**Figure 5** The change of main ions with time in the different chambers. (A) Working chamber; (B) Recovery chamber and cathode chamber. The applied voltage was 1.2 V. The initial concentration of  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and  $\text{Na}^+$  in the synthetic wastewater was 300, 150, 150 and 150 M, respectively.



**Figure 6** The system performance with cattle manure. The applied voltage was 1.2 V.



- Novel bipolar bioelectrodialysis for ammonia and sulfate recovery from wastes.
- Hydrogen production and wastewater treatment were accomplished along with recovery.
- Cathodic gas recirculation increased the nitrogen and sulfate fluxes by 2.3 times.
- The system was affected by the voltage, other ions,  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  concentrations.
- Net energy was produced at all the applied voltages between 0.8 and 1.4 V.

**Supplementary data**

Page: 3; Figure: 1

**Recovery of ammonia and sulfate from waste streams and bioenergy production  
via bipolar bioelectrodialysis**

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## Calculations

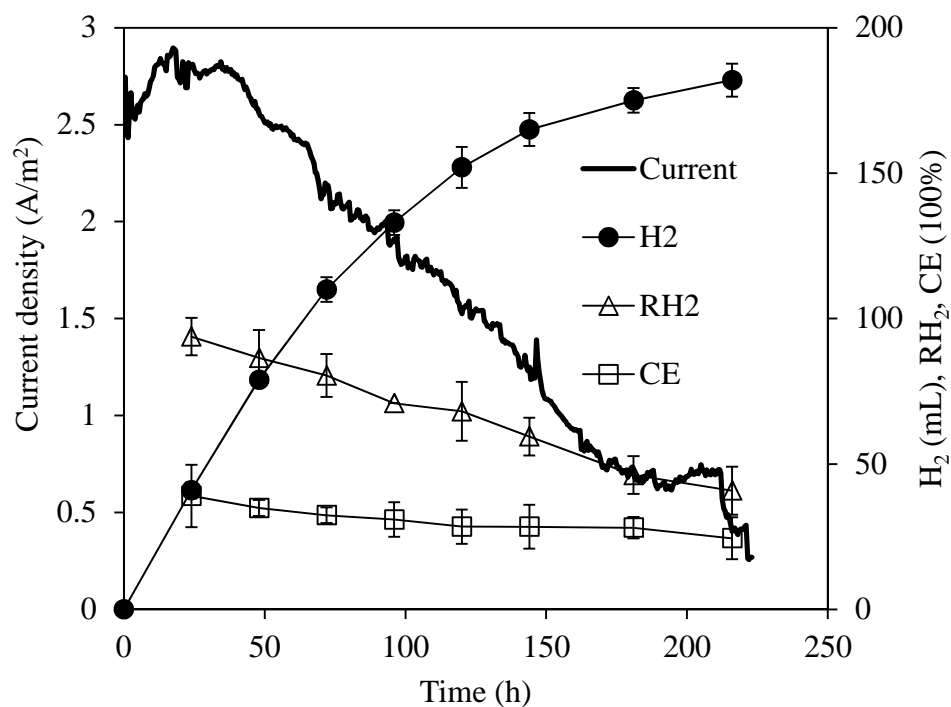
Power requirement by the pump was estimated as<sup>1</sup>:

$$P = \frac{Q\gamma E}{1000}$$

where P is power requirement (kW), Q is flow rate (m<sup>3</sup>/s),  $\gamma$  is 9800 N/m<sup>3</sup>, and E is the hydraulic pressure head (m). For the anolyte recirculation, Q was 8.3×10<sup>-7</sup> m<sup>3</sup>/s (50 mL/min). The measured hydraulic pressure head loss was 0.025 m. Therefore, the power required was 2.03×10<sup>-7</sup> kW for the anolyte recirculation pump. The energy required over the batch test (94 h) was 1.91×10<sup>-5</sup> kWh.

## Reference

1. Xiao, L.; Young, E. B.; Berges, J. A.; He, Z. *Environ. Sci. Technol.* **2012**, *46*, 11459-11466.



**Figure S1** Process performance with the appearance of other ions in the synthetic wastewater. The applied voltage is 1.2 V. The initial concentration of  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and  $\text{Na}^+$  in the synthetic wastewater was 300, 150, 150 and 150 M, respectively.